

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification</b> <sup>6</sup> : <b>C11B 9/00, C11D 3/39, 3/50</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/57233</b> <b>(43) International Publication Date:</b> 11 November 1999 (11.11.99)
<b>(21) International Application Number:</b> PCT/GB99/01401 <b>(22) International Filing Date:</b> 5 May 1999 (05.05.99) <b>(30) Priority Data:</b> 9809772.8                      7 May 1998 (07.05.98)                      GB <b>(71) Applicant (for all designated States except US):</b> QUEST INTERNATIONAL B.V. [NL/NL]; Huizerstraatweg 28, NL-1411 GP Naarden (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CLEMENTS, Christopher, Francis [GB/GB]; 4 Lookers Lane, Saltwood, Hythe, Kent CT21 5HW (GB). PIDDOCK, Christopher, Charles [GB/GB]; 3 Downs Close, Hawkinge, Folkestone, Kent CT18 7PA (GB). PERRING, Keith, Douglas [GB/GB]; 14 Malvern Road, Ashford, Kent TN24 8HS (GB). <b>(74) Agents:</b> HUMPHRIES, Martyn et al.; ICI Group Intellectual Property, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PERFUME COMPOSITION  <b>(57) Abstract</b>  Deodorant perfumes, bleach compositions and bleaching detergent compositions containing such deodorant perfumes. The deodorant perfume is a mixture of fragrance materials having a Malodour Reduction Value of 0.25 to 3.0 and containing at least 55 % by weight of components having a Lipoxidase-Inhibiting Capacity of at least 50 % or a Raoult Variance Ratio of at least 1.1 in the Morpholine Test, or fall within 6 defined chemical classes.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**PERFUME COMPOSITION**

This invention relates to deodorant perfumes, and to bleach compositions and bleaching detergent compositions containing such perfumes.

5 A number of documents, including EP-A-3172 and EP-A-545556 teach that certain perfumes formulated from selected fragrance materials are able to perform a deodorant function. More specifically these documents teach that when such a perfume is incorporated into a detergent composition, and garments are washed with that composition, development of human body malodour will be inhibited when the garments are worn.

10 It is well known to incorporate a bleach into a detergent composition, and it is known that a bleach can damage other ingredients of a detergent composition, including perfume.

Many perfume compositions undergo undesired change or degradation after prolonged storage in a detergent composition containing bleach. This problem has become greater.

15 There have been a number of proposals which address this problem. For example, the bleach active, bleach precursor or both may be encapsulated to eliminate or reduce contact with the perfume. It is known in the art to screen perfume ingredients to identify those which display acceptable chemical stability or olfactory performance during storage in the presence of the bleaching system. This second route was disclosed in WO92/08780 (Procter and  
20 Gamble) and in EP299561 (Unilever), both of which describe stability/performance tests.

EP-A-147191 discloses certain rules for the formulation of deodorant perfume compositions which are resistant to perborate bleach accompanied by N,N,N',N'-tetraacetylene diamine (TAED) as bleach precursor.

Over and above the general problem that detergent compositions present increasing  
25 inherent bleach hostility to perfume, there is the further difficulty that in many countries the ambient conditions place severe additional strain on perfume stability and performance (eg. in many countries it is desirable that the perfume be capable of delivering acceptable performance following storage in bleach laundry powder for 4 weeks or more at temperatures of at least 37 °C, possibly at least 40 or 45 °C, and often with high humidities such as at least  
30 70% relative humidity). Even encapsulation of the bleach system may prove inadequate to prevent perfume decomposition.

According to a first aspect of the present invention, a deodorant perfume composition is a mixture of fragrance materials which gives a Malodour Reduction Value of 0.25 to 3.0 in

a Malodour Reduction Test as set out in EP-A-147191, and comprises at least 55wt% (based on the perfume composition) of a plurality of component materials which:

- have a Lipoxidase-Inhibiting Capacity (LIC value) of at least 50% in the Lipoxidase Test set out in EP-A-147191,
- 5 • or have a Raoult Variance Ratio of at least 1.1 in the Morpholine Test set out in EP-A-147191,
- or are named as components below;

such components each falling within and being allocated to one of six classes as follows:

class 1:

10 phenolic compounds

class 2:

natural essential oils or resins containing less than 20% (by weight of the oil or resin) of phenolic compounds

class 3:

15 aldehydes and ketones

class 4:

polycyclic compounds and nitriles

class 5:

esters

20 class 6:

alcohols and ethers, excluding polyols of molecular weight less than 140;

provided that:

- a) any said component which could be allocated to more than one of the above classes shall be allocated to the class with the lowest number;
- 25 b) any component material which is present in an amount less than 0.5wt% shall not be allocated to any said class;
- c) at least 17wt% of class 3 is present;
- d) at least 5wt% of class 4 is present;
- e) at least 20wt% of class 6 is present;
- 30 f) no more than 15wt% by weight in total of classes 1 and 2 are present. The above percentages by weight are based on the whole perfume composition.

Perfume compositions embodying this invention may be incorporated into bleaching compositions, especially bleaching detergent compositions in solid form, and can deliver good performance following storage under conditions of temperature and humidity.

In a second aspect the invention provides a bleaching composition containing a 5 peroxygen bleach and perfume as set forth above.

Such a bleaching composition may be a bleaching detergent composition containing synthetic (ie. non-soap) detergent in addition to the peroxygen bleach and perfume.

#### Perfume Components

The component materials of the perfume and allocation to classes will now be 10 discussed in greater detail.

Component materials must be among the listed materials below, and/or have an LIC value of at least 50% according to the Lipoxidase test and/or have an RVR value of at least 1.1 according to the Morpholine test. Some component materials have both an LIC value of at least 50% and an RVR value of at least 1.1. These two tests were set out in EP-A-147191 15 and the description of them is repeated here as follows:

#### The Lipoxidase Test

In this test, the capacity of a material to inhibit the oxidation of linoleic acid by lipoxidase (EC1.13.1.13) to form a hydroperoxide is measured.

Aqueous 0.2M sodium borate solution (pH 9.0) is used as a buffer.

20 A control substrate solution is prepared by dissolving linoleic acid (2ml) in absolute ethanol (60ml), diluting with distilled water to 100ml and then adding borate buffer (100ml) and absolute ethanol (300ml).

A test substrate solution is prepared in the same way as the control substrate solution except that for the absolute ethanol (300ml) is substituted the same volume of a 0.5% by 25 weight solution in ethanol of the material to be tested.

A solution of the enzyme lipoxidase in the borate buffer and having an activity within the range of from 15,000 to 40,000 units per ml is prepared.

The activity of the lipoxidase in catalysing the oxidation of linoleic acid is first assayed spectrophotometrically using the control. An automatic continuously recording 30 spectrophotometer is used and the increase in extinction of 234nm (the peak for hydroperoxide) is measured to follow the course of oxidation, the enzyme concentration used being such that it gives an increase in optical density ( $\Delta OD$ ) at 234nm within the range of from 0.6 to 1.0 units per minute. The following materials are placed in two 3ml cuvettes:

4

	<u>Control (ml)</u>	<u>Blank (ml)</u>
Control substrate solution	0.10	0.10
Absolute ethanol	0.10	0.10
Borate buffer	2.75	2.80
5 Lipoxidase solution	0.05	-

The lipoxidase solution is added to the control cuvette last and the reaction immediately followed spectrophotometrically for about 3 minutes, with recording of the increase in optical density at 234nm as a curve on a graph.

- 10 The capacity of a material to inhibit the oxidation is then measured using a test sample containing enzyme, substrate and a deodorant material. The following ingredients are placed in two 3ml cuvettes.

	<u>Test Sample (ml)</u>	<u>Blank (ml)</u>
15 Test substrate solution	0.10	0.10
Absolute ethanol	0.10	0.10
Borate buffer	2.75	2.80
Lipoxidase solution	0.05	-

- 20 The lipoxidase solution is added to the test sample cuvette last and the course of the reaction immediately followed as before.

The lipoxidase-inhibiting capacity of the material is then calculated from the formula  $100 (S_1 - S_2) / S_1$  is the slope of the curve obtained with the control and  $S_2$  is the slope of the curve obtained with the test sample, and thus expressed as % inhibition. A material that gives at least 50% inhibition in the test is hereafter referred to as having a Lipoxidase-Inhibiting Capacity (LIC value) of at least 50%.

#### The Morpholine Test

In this test, the capacity of a material to depress the partial vapour pressure of morpholine more than that required by Raoult's Law is measured. Substances that undergo chemical reaction with morpholine, for example aldehydes, are to be regarded as being excluded from the test.

Morpholine (1g) is introduced into a sample bottle of capacity 20ml and the bottle fitted with a serum cap. The bottle is then incubated at 37 °C for 30 minutes in order to reach

equilibrium. The gas in the headspace of the bottle is analysed by piercing the serum cap with a capillary needle through which nitrogen at 37 °C is passed to increase the pressure in the bottle by a standard amount, the excess pressure then injecting a sample from the headspace into gas chromatograph apparatus, which analyses it and provides a chromatographic trace with a peak due to morpholine, the area under which is proportional to the amount of morpholine in the sample.

The procedure is repeated under exactly the same conditions using instead of morpholine alone, morpholine (0.25g) and the material to be tested (1g); and also using the material (1g) without the morpholine to check whether it gives an interference with the morpholine peak.

The procedure is repeated until reproducible results are obtained. The areas under the morpholine peaks are measured and any necessary correction due to interference by the material is made.

A suitable apparatus which has been used for carrying out the above procedure is a Perkin-Elmer Automatic GC Multifract F40 for Head Space Analysis. Further details of this method are described by Kolb in "CZ-Chemie-Technik", Vol. 1, No. 2, 87-91 (1972) and by Jentzsch et al in "Z. Anal. Chem." 236, 96-118 (1968). Headspace analysis for the morpholine test can also be carried out using other apparatus for sampling and gas chromatography, e.g. a Fisons GC 8000 Series gas chromatograph equipped with an HS 850 headspace autosampler.

The measured areas representing the morpholine concentration are proportional to the partial vapour pressure of the morpholine in the bottle headspace. If A is the area under the morpholine peak when only morpholine is tested and A' is the area due to morpholine when a material is present, the relative lowering of partial vapour pressure of morpholine by the material is given by

$$(1 - A')/A.$$

According to Raoult's Law, if at a given temperature the partial vapour pressure of morpholine in equilibrium with air above liquid morpholine is p, the partial vapour pressure p' exerted by morpholine in a homogenous liquid mixture of morpholine and material at the same temperature is  $pM/(M+PC)$ , where M and PC are the molar concentrations of morpholine and material. Hence, according to Raoult's Law the relative lowering of morpholine partial vapour pressure  $(p-p')/p$ , is given by  $(1-M)/(M+PC)$ , which under the

circumstances of the test is  $87/(87+m/4)$ , where  $m$  is the molecular weight of the perfume material. The molecular weight of morpholine is 87.

The extent to which the behaviour of the mixture departs from Raoult's Law is given by the ratio

$$\frac{(1 - A') / A}{87 / (87 + m / 4)}$$

The above ratio, which will be referred to as the Raoult Variance Ratio, is calculated from the test results. Where a material is a mixture of compounds, a calculated or experimentally determined average molecular weight is used for  $m$ . A material that depresses the partial vapour pressure of morpholine by at least 10% more than that required by Raoult's Law is one in which the Raoult Variance Ratio (RVR value) is at least 1.1.

Perfume materials with the required values of LIC, RVR or both are allocated to one of the six classes, unless they do not fall within the definition of any class, or are present in the perfume composition in small amount, less than 0.5 wt%.

The perfume components which are used may desirably include a number of materials which, in addition to meeting other requirements for components, have a boiling point of 250 °C or above and an octanol/water partition coefficient  $P$  such that  $\log_{10}P$  is 3.0 or above. Such materials have been reported to be substantive to fabrics and to give an enduring fragrance when deposited thereon.

Class 1 is compounds which incorporate a phenolic group, ie. an aromatic ring substituted with hydroxyl on the ring.

Examples of suitable perfume components in class 1 are

	LIC	RVR	Bpt $\geq$ 250°C and logP $\geq$ 3.0
iso-amyl salicylate	95	1.24	yes
benzyl salicylate	0	1.58	yes
carvacrol	32	1.43	
ethyl vanillin	100	1.43	
iso-eugenol	100	1.48	
methyl 2,4-dihydroxy-3,6-dimethyl benzoate [LRG 201]	100	1.21	
thymol			



Some perfume compositions of this invention do not include any material in this class. For some other perfume compositions embodying this invention, it has been found valuable to include a limited amount of such materials, not exceeding 15wt% of the perfume composition and possibly ranging from 1 to 10wt% of the perfume composition.

5 Some natural essential oils contain high proportions of phenolic compounds, and may be included in a perfume composition as a source of such a compound. For example, thyme oil red contains thymol as the largest individual constituent (typically about 25 to 60% by weight of the oil, usually at least 35%).

A preferred group of class 1 materials excludes those with ethylenic or aldehydic 10 unsaturation in substituent groups on the benzene ring.

Class 2 is natural essential oils and resins excluding any which contain more than 20% of phenolic compounds - although oils which contain phenolic compounds may be included in a composition as a source of class 1 materials, as mentioned above.

Some perfume compositions of this invention do not include any material in this class. 15 Other perfume compositions of this invention include some natural oils, but it is preferred to restrict the amount of class 2 essential oils in the composition to not more than 10wt% better not more than 5wt% of the perfume composition.

Examples of essential oils with LIC values greater than 50% or RVR values greater than 1.1 are:

	<b>LIC</b>	<b>RVR</b>
Benzoin Siam Resiniod	87	-
Geranium oil	26	1.29
Opopnax resinoid	96	1.33
Patchouli oil	76	1.25
Petitgrain oil	34	1.27

20 Class 3 is aldehydes and ketones.

Examples of materials in this class are:

	<b>LIC</b>	<b>RVR</b>	<b>Bpt<math>\geq</math>250°C and logP<math>\geq</math>3.0</b>	<b>Preferred subset</b>
6-acetyl-1,1,3,4,4,6-hexamethyl- tetrahydronaphthalene [Tonalid]	100	1.03	yes	yes
p-t-amyl cyclohexanone	50	1.10		

p-t-butyl- $\alpha$ -methyl hydrocinnamic aldehyde	74	--	yes	
2-n-heptylcyclopentanone	56	1.05		
$\alpha$ -iso-methyl ionone	100	1.13	yes	yes
$\beta$ -methyl naphthyl ketone	100	0.96	yes	yes
benzyl acetone				
2,7,8-trimethyl-1-acetyl- cyclododeca-2,5,9-triene [Cyclisone]			yes	yes
1-(1,2,8,8-tetramethyl- 1,2,3,5,6,7,8,8a-octahydro-2- naphthalenyl) -1-ethanone [iso E super]			yes	yes
2,2,7,7-tetramethyl- tricyclo [6.2.1.0 <sup>1,6</sup> ] undecan-5-one [isolongifolanone]			yes	yes
1-(1-isopropyl-1,3,3,6- tetramethyl-2,3-dihydro-1H-5- indenyl)-1-ethanone			yes	yes
1-(3-isopropyl-1,1,2,6- tetramethyl-2,3-dihydro-1H-5- indenyl) -1-ethanone [Traseolide]			yes	yes

It is required in this invention that at least 17wt% of the perfume composition is class 3 material. Preferred is that such material is from 17 to 20 wt% up to 40 or 50 wt% of the perfume composition.

In a preferred composition, at least 17 wt% of the perfume composition is class 3 material selected from those named in the list above. Further preferred is that at least 15 wt%, better at least 17 or 20 wt% of the perfume composition and/or at least 75% by weight of the components in class 3 is selected from the materials indicated to belong to the preferred subset in the right hand column of the table above,

i.e. 6-acetyl-1,1,3,4,4,6-hexamethyl-

10 tetrahydronaphthalene [Tonalid],  $\alpha$ -iso-methyl ionone,  $\beta$ -methyl naphthyl ketone,

2,7,8-trimethyl-1-acetyl-cycododeca-2,5,9-triene [Cyclisone],

1-(1,2,8,8-tetramethyl-1,2,3,5,6,7,8,8a-octahydro-2-naphthalenyl)-1-ethanone [iso E super],

2,2,7,7-tetramethyl-tricyclo [6.2.1.0<sup>1,6</sup>] undecan-5-one [isolongifolanone],

1-(1-isopropyl-1,3,3,6-tetramethyl-2,3-dihydro-1H-5-indenyl)-1-ethanone and,

15 1-(3-isopropyl-1,1,2,6-tetramethyl-2,3-dihydro-1H-5-indenyl)-1-ethanone [Traseolide].

Class 4 is polycyclic compounds and nitriles. Polycyclic compounds are those in which one or more atoms are members of more than one ring, in particular compounds with fused ring systems such as naphthalene and isobornene derivatives. This category includes polycyclic compounds with one or more heteroatoms present in a ring, such as quinoline derivatives.

Examples of materials in class 4 are:

	LIC	RVR	Bpt $\geq$ 250°C and logP $\geq$ 3.0	Preferred subset
iso-butyl quinoline	--	1.10	yes	
coumarin	58	1.22		yes
1,3,4,6,7,8-Hexahydro-4,6,6,7-8, 8-hexamethyl cyclopenta- $\gamma$ -2- benzo-pyran [Galaxolide]	100	--	yes	yes
3a-methyl-dodecahydro-6,6,9a- trimethylnaphtho(2,1-b) furan	58	1.30	yes	
$\beta$ -naphthyl methyl ether [Yara]	100	--	yes	yes
cedryl methyl ether [Cedramber]			yes	
tricyclo [5.2.1.0 <sup>2,6</sup> ]dec-4-en-8- yl propanoate [Florocyclene]			yes	yes
ethyl tricyclo [5.2.1.0 <sup>2,6</sup> ]decane-2- carboxylate [Fruitate]			yes	yes
2-methyldecane nitrile [Fruitonile]				yes

It is required in this invention that at least 5wt% better at least 8 or 10wt% of the perfume composition is class 4 material. Preferred is that such material is from 10 to 40 wt% of the perfume composition.

- 10 In a preferred composition, at least 10 wt% of the perfume composition is class 4 material selected from those named in the list above. Further preferred is that at least 5 or 8 wt% of the perfume composition and/or at least 75% by weight of the components in class 4 is selected from the materials indicated to belong to the preferred subset in the right hand column of the table above.

Class 5 is esters.

Examples of esters in this class are:

	LIC	RVR	Bpt $\geq$ 250°C and logP $\geq$ 3.0
ortho-t-butyl cyclohexyl acetate	52	1.08	yes
para-t-butyl cyclohexyl acetate	54	0.98	yes
diethyl phthalate	79	1.20	yes
nonanediol-1,3-diacetate	33	1.17	yes
Nonanolide-1,4	92	0.87	
i-Nonyl acetate	50	0.83	
i-Nonyl formate	19	1.49	
phenylethyl phenyl acetate	0	1.22	yes
dihydromyrcenyl formate		>1.1	

Preferred embodiments of this invention contain at least 5 wt% better at least 8 wt% of the perfume composition of esters in class 5. The amount of such class 5 esters is typically 5 from 5 wt% up to 20 or 25 wt% of the perfume composition.

In some preferred compositions, at least 5 wt% of the perfume composition is class 5 material selected from those named in the list above.

Class 6 is alcohols and ethers but excludes polyols of molecular weight below 140 such as dipropylene glycol. Such polyols are polar compounds, known for use as carriers, 10 which generally do not themselves deposit on fabric from a wash liquor.

Examples of materials in this class are:

	LIC	RVR	Bpt $\geq$ 250°C and logP $\geq$ 3.0	Preferred subset
cinnamic alcohol	--	1.28		
dihydromyrcenol	--	>1.1		
hydroxymethyl isopropyl cyclohexane [Mayol]	60	1.23		
tetrahydromuguol	24	1.23		
phenyl ethyl alcohol	22	1.24		yes
tetrahydrolinalol		>1.1		yes
1-[(2'-t-butylcyclohexyl) oxy]-butan-2-ol [Amber Core]			yes	yes
1-(ethoxymethoxy) cyclododecane [Boisambrene forte]			yes	yes
phenylethyl isoamyl ether [Anther]				
2-ethyl-4-(2',2'3'-trimethyl- cyclopent-3'-enyl)-but-2-enol [Banalol]		1.26	yes	yes
diphenyl oxide			yes	
3-methyl-5-phenylpentanol [Phenoxanol]			yes	yes
5-(sec-butyl)-2-(2',4'- dimethylcyclohex-3'-enyl)-5- methyl-1,3-dioxane [Karanal]			yes	yes

Dihydromyrcenol in class 6 and dihydromyrcenyl formate in class 5 may be incorporated together as the commercially available material "dimyrcetol" which contains approximately equal amounts of both.

It is required in this invention that at least 20wt% of the perfume composition is class 6 material. Preferred is that such material is from 20wt% up to 50 or 60 wt% of the perfume composition.

10 In a preferred composition, at least 20 wt% of the perfume composition is class 6 material selected from those named in the list above. Further preferred is that at least 15 wt%, better at least 20 wt% of the perfume composition and/or at least 75% by weight of the components in class 6 is selected from the materials indicated to belong to the preferred subset in the right hand column of the table above.

It will be appreciated that a perfume composition of this invention must contain at least one component from each of classes 3,4 and 6 above. Moreover, the total amounts of material(s) in classes 1 and 2 must be less than 15wt% and therefore must be less than the amounts of components in each of classes 3 and 6.

5 It is preferred that the number of component materials is greater than the minimum required to provide components in classes 3, 4 and 6.

Preferably the number of said component materials present in the perfume is at least five, better at least six or seven. It is also preferred that the component materials include at least one material within classes 1, 2 or 5 in addition to materials within classes 3, 4 and 6 so  
10 that the plurality of component materials contains materials allocated to at least four of the six classes. More preferably at least one component material within class 1, class 2 or class 5 is present.

It is preferred that the perfume composition contains at least 70%, even better at least 80% of components falling within the six classes specified above.

15 The balance of the perfume composition may comprise perfume materials which have neither an LIC value of at least 50% nor an RVR value of at least 1.1. It may also comprise materials which by reason of their chemical structure do not fall within any of the six classes, regardless of LIC or RVR value.

Examples of such materials are:

20

	LIC	RVR
citronellyl acetate	18	1.00
linalyl acetate	41	0.83
benzyl acetate	10	1.04
Cedar atlas oil	24	1.08
Caryophyllene	0	0.92
Tarragon	6	1.00
Phenyl ethyl acetate	15	1.03
Undecalactone	33	1.03
Geraniol	34	1.03
phenyl acetic acid		
the oxime of 5-methyl heptan-3-one [Stemone]		

It may be preferred that the entire perfume composition does not contain more than 20% by weight, perhaps not more than 10% by weight, of materials which either are unsaturated materials with two or more ethylenic double bonds, or are phenols with ethylenic unsaturation in substituent groups. Double unsaturated terpenes, terpene alcohols and terpene esters are often present in natural essential oils and synthetic substitutes for such oils.

More restrictively, some perfume compositions of this invention do not contain more than 20wt% of any phenols, terpenes, terpene alcohols, terpene aldehydes or terpene esters with ethylenic unsaturation.

The perfume compositions of this invention give a malodour reduction value of at least 0.25, better at least 0.5 or at least 0.7, in the Malodour Reduction Test, given in EP-A-147,191. This test comprised the steps of:

- (1) selecting pieces of 100% bulked polyester sheet shirt fabric having an area of 20cm x 20cm or more;
- (ii) washing the selected pieces of fabric in a front-loading drum-type washing machine with an unperfumed washing powder: whose composition (in practice the washing powder composition used in the Malodour Reduction test is not critical) is as follows:

	<u>Parts by weight</u>
Sodium dodecylbenzene sulphonate	9
20 C13-15 alcohol 7EO	4
Sodium tripolyphosphate	33
Alkaline sodium silicate	6
Sodium carboxymethyl cellulose	1
Magnesium silicate	1
25 Ethylenediamine tetraacetic acid	0.2
Sodium sulphate	25
Water	10.8

- (iii) rinsing the washed pieces of fabric and drying them to provide "untreated" fabric;
- (iv) re-washing half of the "untreated" pieces of fabric in the washing machine with unperfumed washing powder as above to which had been added 0.25% by weight of a bleach-stable perfume under test, rinsing and re-drying to provide "treated" pieces of fabric;

(v) inserting the "treated" and "untreated" pieces of fabric into clean polyester cotton shirts in the underarm region so that in each shirt, one underarm region received a "treated" fabric insert and the other underarm received an "untreated" fabric insert in accordance with a statistical design;

5 (vi) placing the shirts carrying the inserts on a panel of 40 Caucasian male subjects of age within a range from 20 to 55 years (the subjects being chosen from those who develop axillary body malodour that is not unusually strong and who do not develop a stronger body malodour in one axilla compared with the other);

(vii) assessing the body malodour of the fabric inserts after a period of five hours  
10 whereby three trained female assessors scored the olfactory intensity of malodour on a 0 to 5 scale, 0 representing no odour and 5 representing very strong malodour, the strength of the odour in each instance being related for purposes of comparison to standard odours produced by aqueous solutions of isovaleric acid at different concentrations according to the following table:

Score	Odour Level	Conc. of aqueous isovaleric acid (ml/l)
0	No odour	0
20 1	Slight	0.013
2	Definite	0.053
3	Moderate	0.22
4	Strong	0.87
5	Very Strong	3.57

25

(viii) calculating the average scores for both treated fabric and untreated fabric, and subtracting the average score of the treated fabric from the average score of the untreated fabric to arrive at the Malodour Reduction Value for the perfume composition.

The Malodour Reduction Value can also be expressed as a percentage of the average  
30 score for the untreated fabric.

The perfume compositions of this invention can be incorporated into a bleach composition containing a peroxygen bleach.

Suitable peroxygen bleaching agents may be inorganic peroxygen compounds such as alkali metal perborates, percarbonates and persulphates.



Alternatively, organic peroxyacids can be used, such as peroxy alkanoic acids, diperoxy alkanedioic acids as disclosed in US-A-4337213 and EP-A-254311, phthalimido-perhexanoic acid and other imidoperoxy-carboxylic acids as disclosed in EP-A-325288, EP-A-325289 and EP-A-435379, amidopercarboxylic acids as described in 5 US-A-4634551 and US-A-4686063, and cationic peroxy-carboxylic acids disclosed in US-A-4818426, GB-A-2270690, EP-A-485928 and EP-A-508623.

Some of these bleaching agents, especially the inorganic persalts, are best used together with a bleaching activator which enhances bleaching performance at low temperature. The activator which is most commonly used is N,N,N',N' -tetracetyl ethylene 10 diamine. Others are tetraacetyl glycoluril, pentaacetylglucose, cholyl sulphophenyl carbonate (CSPC), acyloxybenzene sulphonates as described in EP-A-098201, amido-containing compounds described in US-A-4634551 and lactams described in WO 95/00626 and US-A-4545784.

An inorganic persalt and a bleach activator may typically be used in a weight ratio 15 varying from 30:1 to 1:1 preferably from 10:1 to 2:1.

The peroxygen bleach may be encapsulated to improve bleach stability, even though such encapsulation may be unable to provide perfume stability by separation of bleach from perfume.

If peroxygen bleach is the main active ingredient of a composition, it may for 20 example be present as from 20 to 90% by weight of the composition. However, it is particularly envisaged that the perfume compositions of this invention can be incorporated into a bleaching detergent composition to be used for fabric washing.

Such a composition will typically contain from 2 to 50% of non-soap detergent active, from 5 to 80% of detergency builder, from 1 to 40% often from 3 to 30% of peroxygen 25 bleach, and from 0 to 10% of bleach activator, these percentages all being by weight of the bleaching detergent composition.

The balance of the composition, if any, may include various ingredients known for inclusion in fabric washing detergents. A detergent composition for fabric washing may be in solid form, notably in particulate form (detergent powder) or in the form of solid articles (bars 30 or tablets) or may be in liquid form with aqueous, non-aqueous or mixed liquid phases, with or without suspended solid.

The amount of perfume used in a bleaching composition of this invention will generally lie in a range from 0.01% to 5% by weight of the bleaching composition.

A preferred amount of perfume for use in many fabric washing products is from 0.1 to 1%, frequently 0.1 to 0.7% by weight, but where the product is in a concentrated form the amount of perfume may be greater, up to 1.5% or even up to 2% by weight of the product.

As mentioned, the total amount of detergent-active material (surfactant) in bleaching 5 detergent compositions for fabric washing is generally from 2 to 50% by weight. Detergent active is preferably present in a quantity of at least 5% or 10% by weight of a composition, and may well be in a quantity not exceeding 30% or 40% by weight.

Detergent-active materials may be one or more soap or non-soap anionic, nonionic, cationic, amphoteric or zwitterionic surfactants, or combinations of these. Typical of these are 10 the alkyl benzene sulphonates, alkyl sulphonates, alkyl ether sulphates, primary alkyl sulphates, alkoxylated alcohols, alpha-sulphonates of fatty acids and of fatty acid esters, alkyl betaines, and alkyl polyglycosides all known in the detergent art.

Detergency builders are materials which function to soften hard water by solubilisation or other removal of calcium and to a lesser extent magnesium salts responsible 15 for water hardness compounds. A particularly well known group of water soluble detergency builders are the alkali metal phosphates and condensed phosphates, especially exemplified by sodium pyrophosphate and tripolyphosphate. A further water soluble inorganic builder compound is sodium carbonate which is generally used in conjunction with a seed crystal to accelerate the precipitation of calcium carbonate. Organic detergency builders such as 20 sodium citrate and polyacrylate can also be used.

Common insoluble inorganic detergency builders are zeolites. These are normally used jointly with a smaller quantity of a water soluble builder, especially a polycarboxylate which may be a copolymer of acrylate and maleate residues. As is well known, many detergent compositions avoid phosphate builders.

25 The detergency builder component of a detergent composition will as mentioned, generally comprise from 5 to 80%, preferably from 5 or 10% up to 60% by weight of the detergent composition.

A liquid composition will typically contain 5% to 40% by weight of water-soluble builder salt, partially dissolved and partially suspended in an aqueous liquid phase.

30 Other ingredients which are customarily included in a detergent composition, although not necessarily all together, include alkaline silicate, soil release agents, anti-redeposition agents such as sodium carboxymethyl cellulose, enzymes, fabric softening

agents including softening clays, fluorescent brighteners, antifoam agents or conversely foam boosters and filler such as sodium sulphate.

## CLAIMS

1. A deodorant perfume composition which is a mixture of fragrance materials with a  
 Malodour Reduction Value of 0.25 to 3.0 in the Malodour Reduction Test herein, and  
 5 which comprises at least 55% (by weight of the perfume composition) of a plurality of  
 component materials which:
  - have a Lipoxidase-Inhibiting Capacity (LIC value) of at least 50% in the Lipoxidase  
 Test herein,
  - or have a Raoult Variance Ratio of at least 1.1 in the Morpholine Test herein,
  - 10 • or are named as components included in classes below;

such components each falling within and being allocated to one of six classes as follows:

- |    |   |
|----|---|
| 15 | <p>Class 1: phenolic compounds, including iso-amyl salicylate, benzyl salicylate,<br/>         carvacrol, ethyl vanillin, iso-eugenol, methyl 2,4-dihydroxy-3,6-dimethyl<br/>         benzoate [LRG 201] and thymol;</p>  |
|    | <p>Class 2: natural essential oils and resins containing less than 20% (by weight of the oil<br/>         or resin) of phenolic compounds;</p>  |
| 20 | <p>Class 3: aldehydes and ketones, including 6 -acetyl-<br/>         1,1,3,4,4,6-hexamethyl-tetrahydronaphthalene [Tonalid], p-t-amyl<br/>         cyclohexanone, p-t-butyl-<math>\alpha</math>-methyl hydrocinnamic aldehyde,<br/>         2-n-heptylcyclopentanone, <math>\alpha</math>-iso-Methyl ionone, <math>\beta</math>-Methyl naphthyl ketone,<br/>         benzyl acetone, 2,7,8-trimethyl-1-acetyl-cyclododeca-2,5,9-triene [Cyclisone]<br/>         1-(1,2,8,8-tetramethyl-1,2,3,5,6,7,8,8a-octahydro-2-naphthalenyl)-1-ethanone<br/>         25 [iso E super], 2,2,7,7-tetramethyl-tricyclo[6.2.1.0<sup>1,6</sup>]undecan-5-one<br/>         [isolongifolanone]<br/>         1-(1-isopropyl-1,3,3,6-tetramethyl-2,3-dihydro-1H-5-indenyl)-1-ethanone and<br/>         1-(3-isopropyl-1,1,2,6-tetramethyl-2,3-dihydro-1H-5-indenyl)-1-ethanone<br/>         [Traseolide];</p> |
| 30 | <p>Class 4: polycyclic compounds and nitriles, including iso-butyl quinoline, coumarin,<br/>         1,3,4,6,7,8-Hexahydro-4,6,6,7-8,8-hexamethyl cyclopenta-<math>\gamma</math>-2-benzo-pyran<br/>         [Galaxolide], 3a-methyl-dodecahydro-6,6,9a-trimethylnaphtho(2,1-b)furan,<br/> <math>\beta</math>-naphthyl methyl ether [Yara],<br/>         cedryl methyl ether [Cedramber],</p>  |

tricyclo[5.2.1.0<sup>2,6</sup>]dec-4-en-8-yl propanoate [Florocyclene],  
ethyl tricyclo[5.2.1.0<sup>2,6</sup>]decane-2-carboxylate [Fruitate], and  
2-methyldecane nitrile [Frutonile];

Class 5: esters, including ortho-t-butyl cyclohexyl acetate, para-t-butyl cyclohexyl  
5 acetate, diethyl phthalate, nonanediol-1,3-diacetate,

Nonanolide-1,4, i-Nonyl acetate, i-Nonyl formate, phenylethyl phenyl acetate  
and dihydromyrcenyl formate;

Class 6: alcohols and ethers, including cinnamic alcohol, dihydromyrcenol,  
hydroxymethylisopropylcyclohexane [Mayol], tetrahydromuguol, phenylethyl  
10 alcohol, tetrahydrolinalol, 1-[(2'-t-butylcyclohexyl)oxy]-butan-2-ol  
[Amber Core], 1-(ethoxymethoxy)cyclododecane [Boisambrene forte],  
phenylethyl isoamyl ether [Anther],

2-ethyl-4-(2',2',3'-trimethyl-cyclopent-3'-enyl)-but-2-enol [Bangalol], diphenyl  
oxide, 3-methyl-5-phenylpentanol [Phenoxanol] and 5-(sec-butyl)-2-

15 (2',4'-dimethylcyclohex-3'-enyl)-5-methyl-1,3-dioxane [Karanal]

provided that:

a) any said component which could be allocated to more than one of the above classes is  
allocated to the class with the lowest number;

b) any component material which is present in an amount less than 0.5% (by weight of  
20 the perfume composition) shall not be allocated to any said class;

c) at least 17% (by weight of the perfume composition) of class 3 is present;

d) at least 5% (by weight of the perfume composition) of class 4 is present;

e) at least 20% (by weight of the perfume composition) of class 6 is present;

f) no more than 15% in total (by weight of the perfume composition) of classes 1 and 2  
25 are present.

2. A perfume composition according to claim 1 containing at least 20% (by weight of  
the perfume composition) of materials in class 3 selected from:

6-acetyl-1,1,3,4,4,6-hexamethyl-tetrahydronaphthalene [Tonalid],  $\alpha$ -iso-Methyl

30 ionone,  $\beta$ -Methyl naphthyl ketone, 2,7,8-trimethyl-1-acetyl-cyclododeca-2,5,9-triene  
Cyclisone], 1-(1,2,8,8-tetramethyl-1,2,3,5,6,7,8,8a-octahydro-2-naphthalenyl)-  
1-ethanone [iso E super],

2,2,7,7-tetramethyl-tricyclo[6.2.1.0<sup>1,6</sup>]undecan-5-one [isolongifolanone],  
 1-(1-isopropyl-1,3,3,6-tetramethyl-2,3-dihydro-1H-5-indenyl)-1-ethanone and  
 1-(3-isopropyl-1,1,2,6-tetramethyl-2,3-dihydro-1H-5-indenyl)-1-ethanone  
 [Traseolide].

- 5 3. A perfume composition according to claim 1 or claim 2 containing at least 10% (by weight of the perfume composition) of materials in class 4 selected from: coumarin, 1,3,4,6,7,8-Hexahydro-4,6,6,7-8,8-hexamethyl cyclopenta- $\gamma$ -2-benzo-pyran [Galaxolide],  $\beta$ -naphthyl methyl ether [Yara],  
 10 tricyclo[5.2.1.0<sup>2,6</sup>]dec-4-en-8-yl propanoate [Florocyclene], ethyl tricyclo[5.2.1.0<sup>2,6</sup>]decane-2-carboxylate [Fruitate] and 2-methyldecane nitrile [Frutonile].
4. A perfume composition according to claim 1, claim 2 or claim 3 containing at least  
 15 20% by weight of the perfume composition of materials in class 6 selected from: phenyl ethyl alcohol, tetrahydrolinalol, 1-[(2'-t-butylcyclohexyl)oxy]-butan-2-ol [Amber Core], 1-(ethoxymethoxy)cyclododecane [Boisambrene forte], 2-ethyl-4-(2',2',3'-trimethyl-cyclopent-3'-enyl)-but-2-enol [Bangalol],  
 20 3-methyl-5-phenylpentanol [Phenoxanol] and 5-(sec-butyl)-2-(2',4'-dimethylcyclohex-3'-enyl)-5-methyl-1,3-dioxane [Karanal].
5. A perfume composition according to claim 1 containing at least 8 wt% of materials in class 5.  
 25
6. A perfume composition according to any one of the preceding claims wherein the content of natural essential oils in class 2 is not more than 5% (by weight of the perfume composition).
- 30 7. A perfume composition according to any one of the preceding claims wherein the content of unsaturated materials with two or more ethylenic double bonds and of

phenols with ethylenic unsaturation in substituent groups does not total more than 20% by weight of the perfume composition.

8. A perfume composition according to any one of the preceding claims wherein the  
5 content of any phenols, terpenes, terpene alcohols, terpene aldehydes or terpene esters with ethylenic unsaturation does not total more than 20% by weight of the perfume composition.
9. A bleaching composition comprising from 1% to 90% by weight of peroxygen bleach  
10 and from 0.01% to 5% by weight of a perfume composition according to any one of the preceding claims.
10. A bleaching detergent composition comprising  
15 from 2 to 50% by weight of non-soap detergent active, from 5 to 80% by weight of detergency builder,  
from 1 to 40% of peroxygen bleach, and  
and from 0.1% to 2% by weight of a perfume composition according to any one of claims 1 to 8.
- 20 11. A composition according to claim 10 wherein the peroxygen bleach is an organic peroxy acid.
12. A composition according to claim 10 wherein the peroxygen bleach is an inorganic  
25 peroxygen salt and the composition contains from 1 to 10% by weight of a bleach activator.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/01401

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11B9/00 C11D3/39 C11D3/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D C11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 322 308 A (D.C.HOOPER ET AL.) 30 March 1982 (1982-03-30) column 8, line 35 -column 11, line 6 column 12, line 10 claims	1-12
A	WO 97 07780 A (UNILEVER) 6 March 1997 (1997-03-06) page 22, line 6-11 page 23, line 1 -page 26, line 16 claim 1	1-8
A	WO 98 06804 A (BUSH BOAKE ALLEN) 19 February 1998 (1998-02-19) page 9, line 20 -page 12, line 24; claims	1-12
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

4 October 1999

Date of mailing of the international search report

13/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Van Moer, A



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/01401

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 404 470 A (QUEST INTENATIONAL) 27 December 1990 (1990-12-27) page 3, line 18-38 page 4, line 58 -page 5, line 41; claims; examples ---	1-12
A	US 5 554 588 A (J.M.BEHAN ET AL.) 10 September 1996 (1996-09-10) column 1, line 35 -column 6, line 28 column 8, line 14,15 claims ---	1-12
A	EP 0 147 191 A (UNILEVER) 3 July 1985 (1985-07-03) cited in the application page 17, line 9 -page 23, line 38 claims ---	1-12
A	EP 0 299 561 A (UNILEVER) 18 January 1989 (1989-01-18) cited in the application page 2, line 35 -page 3, line 4 claims ---	1-12
A	WO 92 08780 A (PROCTER & GAMBLE) 29 May 1992 (1992-05-29) cited in the application page 20, line 29 -page 24, line 20 claims -----	1-12

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 99/01401

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4322308 A	30-03-1982	GB 1596791 A	26-08-1981
		AT 15979 A	15-12-1986
		AU 521006 B	11-03-1982
		AU 4322379 A	19-07-1979
		BR 7900155 A	14-08-1979
		CA 1129775 A	17-08-1982
		DE 2900722 A	19-07-1979
		DK 65978 A	13-07-1979
		EP 0003171 A	25-07-1979
		ES 476678 A	16-12-1979
		FI 780439 A	13-07-1979
		FR 2414552 A	10-08-1979
		GB 2013706 A,B	15-08-1979
		HK 42284 A	18-05-1984
		JP 54102309 A	11-08-1979
		MY 10884 A	31-12-1984
		NL 7900210 A	16-07-1979
		NZ 189333 A	31-05-1984
		SE 438325 B	15-04-1985
		SE 7801712 A	13-07-1979
		SG 5183 G	17-02-1984
		US 4289641 A	15-09-1981
		ZA 7900126 A	27-08-1980
		AR 216666 A	15-01-1980
		AT 100478 A	15-12-1980
		AT 375091 B	25-06-1984
		AT 104378 A	15-11-1983
		AT 363194 B	10-07-1981
		AU 515073 B	12-03-1981
		AU 3277078 A	02-08-1979
		AU 519121 B	12-11-1981
		AU 3277178 A	02-08-1979
		AU 514073 B	12-03-1981
		BE 863772 A	08-08-1978
		BE 863773 A	08-08-1978
		BR 7800886 A	02-01-1979
		BR 7800887 A	02-01-1979
		CA 1102243 A	02-06-1981
		CA 1102967 A	16-06-1981
		CH 633313 A	30-11-1982
		CH 635384 A	31-03-1983
		DE 2805767 A	17-08-1978
		DE 2805768 A	17-08-1978
		DK 65778 A,B,	16-08-1978
		DK 65878 A,B,	16-08-1978
		FI 780441 A	16-08-1978
		FI 780442 A	16-08-1978
		FR 2380341 A	08-09-1978
		FR 2393847 A	05-01-1979
		GR 65946 A	09-01-1981
WO 9707780 A	06-03-1997	AU 6927396 A	19-03-1997
		CA 2226212 A	06-03-1997
		CN 1193905 A	23-09-1998
		CZ 9800530 A	15-07-1998
		EP 0845980 A	10-06-1998
		HU 9802412 A	29-03-1999
		PL 325162 A	06-07-1998

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/01401

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9806804 A	19-02-1998	US 5942153 A AU 4064497 A	24-08-1999 06-03-1998
EP 404470 A	27-12-1990	CA 2019222 A,C DE 69008048 D DE 69008048 T ES 2055329 T JP 2746735 B JP 3054300 A US 5501805 A US 5482635 A	19-12-1990 19-05-1994 03-11-1994 16-08-1994 06-05-1998 08-03-1991 26-03-1996 09-01-1996
US 5554588 A	10-09-1996	CA 2082281 A,C DE 69221087 D DE 69221087 T EP 0545556 A ES 2104850 T JP 5255689 A MX 9206423 A ZA 9208578 A	09-05-1993 04-09-1997 13-11-1997 09-06-1993 16-10-1997 05-10-1993 01-05-1993 06-05-1994
EP 147191 A	03-07-1985	AT 46917 T AU 575100 B AU 3688884 A BR 8406656 A CA 1253084 A ES 538846 A GB 2151669 A,B GR 82517 A JP 3057960 B JP 60155298 A JP 2706410 B JP 6122895 A PH 23109 A PT 79733 A,B TR 22858 A US 4663068 A	15-10-1989 21-07-1988 04-07-1985 22-10-1985 25-04-1989 16-06-1987 24-07-1985 08-04-1985 03-09-1991 15-08-1985 28-01-1998 06-05-1994 19-04-1989 01-01-1985 16-09-1988 05-05-1987
EP 299561 A	18-01-1989	AU 613929 B CA 1325601 A DE 3854877 D DE 3854877 T ES 2081802 T JP 1031897 A JP 2524197 B TR 24569 A US 4923631 A	15-08-1991 28-12-1993 22-02-1996 27-06-1996 16-03-1996 02-02-1989 14-08-1996 22-11-1991 08-05-1990
WO 9208780 A	29-05-1992	AT 133195 T AU 9053891 A CA 2096254 A,C CN 1062375 A DE 69116572 D DE 69116572 T EP 0557419 A ES 2082445 T JP 6502669 T MX 9102021 A	15-02-1996 11-06-1992 15-05-1992 01-07-1992 29-02-1996 19-09-1996 01-09-1993 16-03-1996 24-03-1994 29-04-1994

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/01401

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9208780 A		NZ 240572 A	22-12-1994
		PT 99511 A	30-09-1992
		TR 26092 A	15-12-1994
<hr/>			